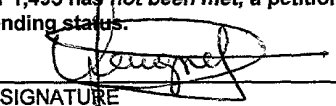


**EXPRESS MAIL LABEL NUMBER EL619400426US**

Form PTO-1390 REV.10-94)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEYS DOCKET NUMBER <b>RN98105</b>
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/elected office (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. (IF KNOWN, SEE 3737 CFR 1.9) <b>09/744497</b> NOT APPLICABLE	
INTERNATIONAL APPLICATION NO. <b>PCT/FR99/01858</b>	INTERNATIONAL FILING DATE <b>July 28, 1999</b>	PRIORITY DATE CLAIMED <b>July 29, 1998</b>	
TITLE OF INVENTION <b>ISOCYANATE COMPOSITION COMPRISING A MASKED ISOCYANATE AND A NONMASKED AND THEIR USE IN A COATING</b>			
APPLICANT (S) FOR DO/EO/US: <b>Jean-Marie BERNARD and Bernard VOGIN</b>			
Applicant herewith submits the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<p>1 <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U S C 371</p> <p>2 <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U S C 371</p> <p>3 <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U S C 371) (f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U S C 371 (b) and PCT Articles 22 and 39(1)</p> <p>4 <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date</p> <p>5 <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U S C 371(c)(2))</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</p> <p style="margin-left: 20px;">b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US)</p> <p>6 <input checked="" type="checkbox"/> A translation of the International Application into English (35 U S C 371(c)(2)).</p> <p>7 <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210)</p> <p>8 <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U S C 371(c)(2)).</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> have been transmitted by the International Bureau</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> have not been made, however the time limit for making such amendments has NOT expired.</p> <p style="margin-left: 20px;">d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>9 <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U S C 371(c)(3)).</p> <p>10 <input checked="" type="checkbox"/> A oath or declaration of the inventor(s) (35 U S C 371(c)(4)). (<b>SIGNED</b>)</p> <p>11 <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</p> <p>12 <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U S C 371(c)(5)).</p> <p><b>Items 13 to 18 below concern document(s) or information included:</b></p> <p>13 <input checked="" type="checkbox"/> An information Disclosure Statement under 37 CFR 1 97 and 1 98</p> <p>14 <input type="checkbox"/> An assignment document for recording A separate cover sheet in compliance with 37 CFR 3 28 and 3 31 is included</p> <p>15 <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment</p> <p>16 <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment</p> <p>17 <input type="checkbox"/> A substitute specification.</p> <p>18 <input type="checkbox"/> A change of power of attorney and/or address letter</p> <p>19 <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail</p> <p>20 <input checked="" type="checkbox"/> Other items or information</p>			
Forms PCT/IB/308 and 332, PCT/ISA/210 (English & French Version), PCT/IPEA/ 409 & 416 PCT/FR99/01858 as published			

US APPLICATION NO. (IF KNOWN, SEE 37 CFR 15) <div style="font-size: 1.5em; font-weight: bold; margin-top: 10px;">09/744497</div>	International Application No. <b>PCT/FR99/01858</b>	ATTORNEY DOCKET NUMBER <b>RN98105</b>
		CALCULATIONS PTO ONLY
21 The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b> <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1,482) nor International search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... \$1,000.00  <input checked="" type="checkbox"/> International preliminary examination fee not paid to USPTO but International Search Report prepared by the EPO or JPO..... \$ 860.00  <input type="checkbox"/> International preliminary examination fee (37 CFR 1,482) not paid to USPTO but international search (37 CFR 1,445 (a)(2)) fee paid to USPTO..... \$ 710.00  <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1,482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$ 690.00  <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1,482) and all claims satisfied provisions of PCT Article 33(2)-(4) ..... \$ 100.00 <div style="text-align: center; font-weight: bold;">ENTER APPROPRIATE BASIC FEE AMOUNT =</div>		
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1,492(e)).		\$ 860.00 <hr/> \$ 0.00
CLAIMS	NUMBER FILED	NUMBER EXTRA
Total Claims	22-20=	2
Independent Claims	1-3=	0
MULTIPLE DEPENDENT CLAIMS(S) (if applicable) N/A <input type="checkbox"/>		\$ 0.00
TOTAL OF ABOVE CALCULATIONS =		\$ 896.00
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) <input type="checkbox"/>		\$ 0.00
SUBTOTAL =		\$ 896.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1,492 (f)).		\$ 0.00
TOTAL NATIONAL FEE =		\$ 896.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + <input type="checkbox"/>		\$ 0.00
TOTAL FEES ENCLOSED =		\$ 896.00
		Amount to be refunded \$
		charged \$
a <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed  b <input checked="" type="checkbox"/> Please charge my Deposit Account No. <b>18-1171</b> in the amount of <b>\$896.00</b> to cover the above fees.  c <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <b>18-1171</b> A duplicate copy of this sheet is enclosed.		
NOTE: Where an appropriate time limit under 37 CFR 1,494 or 1,495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.		
SEND ALL CORRESPONDENCE TO: <b>Jean-Louis SEUGNET</b> <b>RHODIA INC.</b> 259 Prospect Plains Road CN 7500 Cranbury, NJ 08512		<div style="text-align: center;">           SIGNATURE       </div> <div style="text-align: center; margin-top: 10px;"> <b>Jean-Louis SEUGNET</b>          NAME          Limited Recognition under 37 CFR § 10.9(b)          enclosed.       </div> <div style="text-align: center; margin-top: 10px;">         REGISTRATION NUMBER       </div>
January 24, 2001 DATE		

09/744497

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500 Rec'd PCT/PTO 2 4 JAN 2001

Case RN98105

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**In the Application of: Jean-Marie BERNARD, and Bernard VOGIN**

**National Phase of PCT/FR99/01858**

**International Filing Date : July 28, 1999**

**Serial No: N/A**

**Filing Date:**

**For: ISOCYANATE COMPOSITION COMPRISING A MASKED  
ISOCYANATE AND A NONMASKED AND THEIR USE IN A COATING**

Assistant Commissioner for Patents  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT**

Dear Sir:

Prior to calculation of filing fee, please enter the following amendment in the specification and claims:

In the specification:

On page 1, second line of the title, please delete: "[LACUNA]".

Page 1, just after the title, please add: - - This application is an application under 35 U.S.C. Section 371 of International Application Number PCT/FR99/01858 filed on July 28, 1999.- -

In the claims:

Please cancel claims 1 to 17 and add the following new claims 18 to 39:

18. An isocyanate composition comprising a masked isocyanate compound and a nonmasked cycloaliphatic isocyanate compound.

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**Preliminary Amendment**  
**PCT/FR99/01858**

19. A composition as claimed in claim 18, wherein said masked isocyanate compound is at least partially aliphatic.
20. A composition as claimed in claim 18, wherein said masked isocyanate compound exhibits an aliphatic backbone which comprises, in said backbone, at least one di- or polymethylene linkage.
21. A composition as claimed in claim 18, wherein said masked isocyanate compound does not exhibit masked isocyanate functional groups which are carried by an endocyclic cycloaliphatic carbon.
22. A composition as claimed in claim 18, wherein said masked isocyanate compound results from a polymethylene diisocyanate monomer, from one of the (co)oligomers of the latter or from one of its (co)oligocondensates.
23. A composition as claimed in claim 22, wherein said polymethylene diisocyanate monomer is tetra-, penta- or hexamethylene diisocyanate, substituted at the most once.
24. A composition as claimed in claim 18, wherein said (co)oligomer or (co)oligocondensate comprises at least one imidazolidinedione, isocyanuric, biuret, allophanate or polyol carbamate functional group.
25. A composition as claimed in claim 18, wherein said nonmasked cycloaliphatic isocyanate exhibits a Tg at least equal to about 40°C.
26. A composition as claimed in claim 18, wherein said cycloaliphatic isocyanate is an oligomer of a cycloaliphatic monomer.

27. A composition as claimed in claim 18, wherein said cycloaliphatic isocyanate results from the homo- or from the heterotrimerization of a cycloaliphatic monomer.
28. A composition as claimed in claim 18, wherein at least one or two isocyanate functional groups are distant from the closer ring by at most one carbon and are optionally connected directly to it.
29. A composition as claimed in claim 18, wherein said nonmasked isocyanate compound exhibits at least one or two isocyanate functional groups which are a secondary, tertiary or neopentyl isocyanate functional group.
30. A composition as claimed in claim 18, wherein the unmasked isocyanate compound and the masked isocyanate compound present a ratio by mass: unmasked isocyanate compound/ masked isocyanate of at least equal to 0.1.
31. A composition as claimed in claim 30, wherein the ratio is at least equal to 0.3.
32. A composition as claimed in claim 18, wherein the unmasked isocyanate functional groups and the masked isocyanate functional groups present a ratio in equivalents: unmasked isocyanate compound/ masked isocyanate of at most equal to 1.
33. A composition as claimed in claim 32, wherein the ratio is at least equal to 0.7.
34. A process for the preparation of a composition as defined in claim 18, wherein the unmasked isocyanate is mixed in the molten masked isocyanate.
35. A composition as defined in claim 18, further comprising cycloaliphatic compounds with a glass transition temperature (T<sub>g</sub>) at least equal to 40°C for raising the glass transition temperature (T<sub>g</sub>) of the masked aliphatic isocyanate.
36. A painting composition, comprising a composition as defined in claim 18.

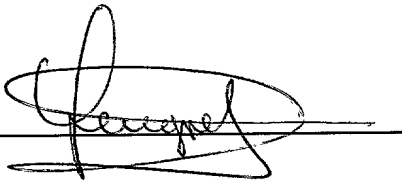
**RN98105**  
**Preliminary Amendment**  
**PCT/FR99/01858**

37. A coating composition, comprising a composition as defined in claim 18.
38. A painting composition, as claimed in claim 36 in the form of a powder.
39. A coating composition, as claimed in claim 37 in the form of a powder.

**REMARKS**

It is asserted that these amendments do not add new matter. Support for these amendments can be found in the specification and claims as originally filed. Entry of these amendments is respectfully requested.

Respectfully submitted,

By 

January 24, 2001

RHODIA INC.  
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F/Brevet/RN98105..prelim

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1

**ISOCYANATE COMPOSITION COMPRISING A MASKED ISOCYANATE  
AND A NONMASKED [LACUNA] AND THEIR USE IN A COATING**

A subject matter of the present invention is  
5 a novel family of isocyanate compositions comprising  
both masked isocyanates and nonmasked isocyanates. It  
relates more particularly to isocyanate compositions  
for the purpose of their use in the powder form,  
including in the form of a mixture of powders, more  
10 specifically for forming paint powders referred to as  
single-component powders (sometimes denoted by the name  
"one shot").

For reasons related to environmental  
protection and work safety, attempts are increasingly  
15 being made to eliminate the use of solvents in coating  
techniques and in particular in painting techniques.  
More particularly, the reduction in V.O.C.s (volatile  
organic compounds) is an increasingly current  
preoccupation in the paint and varnish industry.

20 With this aim, the change in products towards  
higher solid contents makes it possible to reduce the  
amounts of solvents needed to achieve the applicational  
viscosity and thus to reduce the solvents evaporated  
during the drying of the paint film.

25 An alternative to this technique is the use  
of aqueous-phase products where water has replaced  
organic solvents as agent for conveying the organic

binder. However, an amount of organic solvent, admittedly a low amount, remains necessary for the processing and for the formation of the paint film. Furthermore, they generate water-soluble residues, the  
5 treatment of which can be problematic and expensive.

In this context, techniques for coating by means of powder have been increasingly developed. It is advisable here to briefly describe this technique in order to get a better understanding of the present  
10 invention.

The technique employs a very fine pulverulent material for which air will act as carrier.

Generally, an electrostatic charge of several kilovolts applied between a spray gun and the item to  
15 be painted will make it possible to attract and to retain the precursor powder of the coating, which powder will be sprayed out by the applicational spray gun.

Once covered with powder, the item is  
20 subjected to baking, generally at a temperature of between 150 and 200°C, which baking will make possible the melting, the spreading and then the crosslinking of the paint powder in order to obtain a uniform homogeneous layer of the coating. Here and in the  
25 continuation of the description, paint will be regarded as the paradigm of the coatings.



This technique is nonpolluting and exhibits an applicational yield in the vicinity of 100% by virtue of the possibility of recycling the unused powder. For further details on powder paint techniques,

5 reference may be made to the following works:

P. Grandou and P. Pastour: Peintures and Vernis [Paints and Varnishes].

- I. Constituents
- II. Technique and industries;

10 published by Hermann;

R. Lambourne:

Paints and Surface Coatings, Theory and practice; published by Halsted Press;

15 Powder Coating, The Complete Finisher Handbook; The Powder Coating Institute;

Myers and Long;

Treatise on Coatings, 5 volumes;  
published by Marcel Dekker.

Mention should be made, among the families of  
20 products which can be employed in the field of powders,  
of the following. Most of the market is taken up by  
epoxy-polyester powder dyes referred to as "hybrid"  
epoxy-polyester powder dyes, followed by polyesters,  
polyurethanes and then powders referred to as "epoxy"  
25 powders. If high quality exterior behavior (in  
particular with respect to actinic and atmospheric  
attacks) is desired, it is then advisable to use

coatings based on TGIC-polyesters or else on polyurethanes, which alone make it possible to achieve the performances usually required.

However, the TGIC-polyester system is  
5 supposed to be toxic and regulatory restrictions are about to very considerably restrict their use.

As regards polyurethanes, the only powder products currently on the market are products which result from a system in which the crosslinking agent is  
10 an isocyanate masked by caprolactam of a very specific type, namely IPDI derivatives.

However, the use as crosslinking or curing agent of IPDI derivatives does not always result in products of good mechanical property. In a prior patent  
15 application (EP 680 984), the Applicant Company discloses a system with a blocking agent which makes it possible to significantly widen the family of aliphatic isocyanates which are capable of giving solid products with a sufficient Tg (glass transition temperature) to  
20 make possible use in powder applications.

This technique has led, with the collaboration of the Catalan company Resisa (now Cray Valley Ibérica), to a matt or satin painting system with a particularly outstanding performance (see the  
25 International Patent Application published under No. WO 98/04 608).

However, in order to have a sufficient glass transition temperature, the products disclosed in European Patent Application No. EP A 0 680 984 must meet fairly strict restrictions relating to residual  
5 isocyanate functional group content.

In addition, the products disclosed in the abovementioned European Application only represent a small fraction of the masking agents which can be used and which it would be pleasant to be able to employ in  
10 the powder paint technique. There is consequently a search for techniques which make it possible to increase the glass transition temperature of the crosslinking agents, sometimes also known as curing agents.

15 Thus, one of the aims of the present invention is to provide a technique and compositions which make it possible to obtain isocyanate compositions which can be used in powders and which exhibit a glass transition temperature which prevents  
20 phenomena of caking during transportation and storage.

Another aim of the present invention is to provide a technique which makes it possible to increase the glass transition temperature of masked aliphatic isocyanates, so as to be able to use them in  
25 applications referred to as "powder paint" applications.

Another aim of the present invention is to provide isocyanate mixtures with a Tg at least equal to 20°C (advantageously two significant figures), preferably to 25°C and more preferably to 30°C.

5           Another aim of the present invention is to provide isocyanate compositions capable of exhibiting high free isocyanate contents which can be used in powder paints.

          These aims and others which will become  
10   apparent subsequently are achieved by means of an isocyanate composition comprising both a masked isocyanate compound and a nonmasked cycloaliphatic isocyanate compound.

          The present invention is based on a two-fold  
15   observation, namely that it is possible to use isocyanates exhibiting free isocyanate functional groups in powder paint without restrictive operating conditions, provided that they are mixed with a significant amount of masked isocyanate functional  
20   groups.

          The other observation is that the increase in content of free isocyanates makes it possible, under certain conditions, to significantly increase the glass transition temperature.

25           These two observations are particularly surprising to a person skilled in the art.

The invention is particularly advantageous in the case of masked isocyanates with an aliphatic nature. In the present description, any isocyanate functional group in which the nitrogen atom is  
5 connected to a carbon atom with  $sp^3$  hybridization is regarded as aliphatic.

According to the present invention, the masked isocyanate, pure or as a mixture, results from a polyisocyanate, that is to say having at least two  
10 isocyanate functional groups, advantageously more than two (possibility of a fractional value since it is generally a more or less condensed mixture of oligomers), which itself generally results from a precondensation or from a prepolymerization of unit  
15 diisocyanates (sometimes these unit diisocyanates are denoted in the present description by the term "monomers").

These prepolymers and these precondensates are well known to a person skilled in the art and it  
20 may be indicated that, generally, the average molecular mass ( $M_w$ ) of these prepolymers or these precondensates is low and is generally at most equal to 2000 (one significant figure), more commonly to 1 000 (one significant figure, preferably two). Thus, mention may  
25 be made, among the polyisocyanates used to synthesize the masked isocyanates according to the invention, of those of the biuret type and those which, by their di-

or trimerization reaction, have resulted in 4-, 5- or 6-membered rings. Mention may be made, among 6 rings, of the isocyanuric rings resulting from a homo- or from a heterotrimerization of various diisocyanates, alone, with other isocyanates or with carbon dioxide gas; in this case, a nitrogen of the isocyanuric ring is replaced by an oxygen. Oligomers with an isocyanuric ring are preferred. The preferred polyisocyanates are those which exhibit at least one aliphatic isocyanate functional group, advantageously two, preferably all.

Among the masked isocyanate functional groups according to the invention, those which are connected to the backbone via an aliphatic carbon (that is to say of  $sp^3$  type) carrying one hydrogen atom, advantageously two, are preferred.

It is also desirable for the said carbon of  $sp^3$  type to be itself carried by a carbon of  $sp^3$  type, itself also carrying one or preferably two hydrogen atoms, in order to avoid the isocyanate functional group under consideration being in the neopentyl position.

In other words, it is advisable to choose, as monomers (which generally carry two isocyanate functional groups), at least one compound which carries at least one aliphatic functional group which is neither secondary nor tertiary nor neopentyl.

The problem of the masked isocyanates exhibiting a particularly low glass transition temperature is particularly acute in the case where use is made of monomers which exhibit a high conformational freedom and high rotational freedoms.

This is the case with the monomers which exhibit polymethylene  $(CH_2)_\pi$  linkages, where  $\pi$  represents an integer from 2 to 10, advantageously from 4 to 8. These polymethylene linkages result in excellent mechanical properties. In addition, it is desirable for at least one, preferably all, [lacuna] these linkages to be free to rotate and thus exocyclic.

In the case of a mixture obtained from several (in general two) types of monomers, it is preferable for that or those of the monomers which corresponds to the above conditions and in particular to the condition with regard to the presence of polymethylene  $(CH_2)_\pi$  linkages to represent at least one third, advantageously half, preferably two thirds of the masked isocyanate functional groups.

Of course, the results are particularly good when all of the monomer used exhibits this characteristic of having polymethylene linkages.

The above restrictions are applicable both in the case of prepolymers or of precondensates obtained from a mixture of monomers and of prepolymers and of

precondensates obtained by simple mixing of prepolymers and of precondensates.

The present invention is particularly advantageous for masked isocyanates with a  $T_g$  at most equal to  $40^\circ\text{C}$ , advantageously at most equal to  $30^\circ\text{C}$ , preferably at most equal to  $20^\circ\text{C}$ , more preferably of less than  $20^\circ\text{C}$ .

Thus, the present invention is particularly advantageous for masked isocyanates which do not exhibit masked isocyanate functional groups which are carried by an endocyclic cycloaliphatic carbon. This is because these masked isocyanates often naturally exhibit glass transition temperatures which are greater than those of masked non-cycloaliphatic isocyanates, in particular resulting from polymethylene diisocyanate.

Thus, the invention exhibits numerous advantages for polymethylene diisocyanate derivatives, among which may be mentioned hexamethylene diisocyanate, tetramethylene diisocyanate and a hexamethylene diisocyanate isomer, namely pentamethylene diisocyanate substituted by a methyl.

The masked isocyanates result from free isocyanates by reaction with various masking agents.

The masking agents which are particularly suitable for the present invention are those which, in the octanol test, exhibit a release temperature at least equal to  $100^\circ\text{C}$ , advantageously to  $110^\circ\text{C}$ ,



preferably to 120°C. The release temperature is advantageously at most equal to 200°C, preferably 180°C.

The masked isocyanates according to the present invention can be masked by several masking agents. Mention should be made, among masking agents, of triazole, its derivatives and the various compounds mentioned in the patents cited in the present application.

10 The nonmasked isocyanates according to the present invention exhibit an aliphatic ring. It is also desirable for them to be chosen from compounds with a glass transition temperature at least equal to approximately 40°C.

15 The compounds which are particularly well suited are the oligomers or the oligocondensates of cycloaliphatic monomers, that is to say the backbone of which comprises an aliphatic ring. Among these products, those which are preferred are those which  
20 result from the homo- or from the heterotrimerization of a cycloaliphatic monomer.

These monomers are advantageously such that at least one, advantageously both, [lacuna] isocyanate functional groups are distant from the closest ring by  
25 at most one carbon and preferably is connected directly to it. In addition, these cycloaliphatic monomers advantageously exhibit at least one, preferably two,

isocyanate functional groups chosen from secondary, tertiary or neopentyl isocyanate functional groups.

The best results are obtained when the conformational freedom of the cycloaliphatic monomer is low. Mention may be made, as monomers capable of giving good results, of, by way of example and even of paradigm, the following monomers:

- ♦ the compounds corresponding to the hydrogenation of the aromatic nucleus or nuclei carrying isocyanate functional groups of aromatic isocyanate monomer and in particular of TDI (toluene diisocyanate) and of diisocyanatobiphenyls, the compound known under the abbreviation H<sub>12</sub>MDI and the various BICs [Bis(isocyanatomethylcyclohexane)];

and in particular

- ♦ norbornane diisocyanate, often known by the abbreviation NBDI;

- ♦ isophorone diisocyanate or IPDI or 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate.

In order to obtain an effect on the increase in glass transition temperature of the composition, it is preferable for the (FI/MI) ratio by mass of the free isocyanate compound(s) to the masked isocyanate compound(s) to be at least equal to 0.1, advantageously to 0.2, preferably to 0.3.

On the other hand, in order to maintain the qualities related to the masked isocyanates (in part at

least noncyclic isocyanates), it is preferable for the (FIF/MIF) ratio in equivalents of the free isocyanate functional groups to the masked isocyanate functional groups to be at most equal to approximately 1, advantageously to 1.0, preferably to 0.7.

The compositions according to the present invention can easily be prepared by mixing the free isocyanate in the molten masked isocyanate (see the procedure in the examples), advantageously at a temperature of less than that of the deblocking.

The presence of a catalyst for condensation between the masking agents and the isocyanates is not harmful in any way. This is particularly true for tertiary amines (in a ratio of 0.1 to 5% in molar equivalents with respect to the combined masked and nonmasked isocyanate functional groups), which are often used as catalyst.

The present application is also targeted at the use, according to the techniques specified above, of the cycloaliphatic compound with a glass transition temperature at least equal to 40°C for raising the glass transition temperature of masked aliphatic isocyanates.

#### **OCTANOL TEST - Definitions**

25 "Release" (or "deblocking") This is the lowest temperature: temperature at which the masking agent of the

5 masked isocyanate is 9/10  
(mathematically rounded-off) displaced by a  
primary monoalcohol (the  
primary alcohol is  
generally octanol).

Shelf life: In order to ensure a good  
shelf life, it is  
preferable to choose  
10 masked isocyanate  
functional groups for  
which the octanol test  
shows a "release" at  
80°C, advantageously at  
15 90°C, at most equal to  
90%.

Progress of the reaction: The reaction is  
considered to be complete  
if it is carried out to  
20 more than 90%.

#### **PROCEDURE**

Approximately 5 mmol of protected masked NCO  
equivalent to be evaluated are charged to a Schott-type  
tube with magnetic stirring.

25 2.5 to 3 ml of 1,2-dichlorobenzene (solvent)  
[lacuna] the equivalent of 1-octanol (5 mmol, i.e.

0.61 g, and optionally with the catalyst to be tested with the masking group) are added.

The reaction medium is subsequently brought to the test temperature. Heating is then carried out for 6 h at the test temperature, so as to deblock and thus render reactive the isocyanate functional groups. On completion of the reaction, the solvent is removed by vacuum distillation and the residue is analyzed by NMR, mass and infrared [lacuna].

The percentage of masked isocyanate functional groups condensed with the 1-octanol is evaluated from these data.

The following nonlimiting examples illustrate the invention.

Examples of powder syntheses with free NCO IPDT.

**Example 1 - Synthesis of a powder polyisocyanate composition (triazole-blocked HDT/IPDT (70/30 weight/weight))**

290 g of hexamethylene diisocyanate trimer (Tolonate HDT) (NCO content: 0.521 equivalent/100 g), 107.5 g of 1,2,4-triazole and 3.98 g of triethylamine (1% by mass with respect to all the compounds/2.6 molar% with respect to the free NCO functional groups of the HDT) are successively added to a stirred jacketed reactor. The reaction medium is heated to

95°C. The reaction is exothermic and the temperature of the reaction medium rises to 125°C. The temperature gently falls back to 95°C. After 1 h 30, infrared analysis of a withdrawn sample shows that all the isocyanate functional groups are blocked by the triazole. 170.5 g of isophorone diisocyanate trimer (IPDT) (NCO content: 0.45 equivalent/100 g) are then added at 110°C. After mixing for a quarter of an hour, the product is cast and then milled to give 568 g of a white powder with a Tg of 34°C which is stable on storage.

The composition thus comprises an HDT polyisocyanate with isocyanate functional groups which are masked by a single blocking agent and a cycloaliphatic polyisocyanate with free isocyanate functional groups.

**Example 2 - Synthesis of a powder polyisocyanate composition (HDT blocked with triazole/para-hydroxybenzoic acid (80/20 mol/mol)/IPDT (70/30 weight/weight))**

(TOL 6598)

201.84 g of Tolonate HDT, 58.11 g of 1,2,4-triazole and 33.41 g of para-hydroxybenzoic acid are successively added to a stirred 500 ml jacketed reactor. The reaction mixture is heated to 90°C. After reacting for one hour, 2.93 g of triethylamine are added. After 1 h 30, infrared analysis of a withdrawn

sample shows that all the isocyanate functional groups are blocked by the triazole. 125.73 g of isophorone diisocyanate trimer are then added at 110°C. After mixing for 1 h, the product is cast and then milled to give 420 g of a white powder with a Tg of 45°C (i.e. 20°C more than the product to which IPDT has not been added) which is stable on storage.

The composition thus comprises an HDT polyisocyanate with isocyanate functional groups masked by a system of blocking agents, one of which comprises a carboxylic acid functional group, and a cycloaliphatic polyisocyanate with free isocyanate functional groups.

The absorption spectra show NCO, amide and anhydride functional groups.

Everything happens as if the masked isocyanate protected or stabilized the nonmasked isocyanate.

**Example 3 (comparative) - Triazole-masked HDT**

The following are successively charged to a 250 ml reactor

- 107.5 g of hexamethylene diisocyanate isocyanurate trimer known under the trade name HDT, the content of isocyanate (NCO) functional groups of which is 0.526 mol of NCO functional groups per 100 g of product,

- 39.3 g of 1,2,4-triazole (with a purity equal to 99.5%).

The reaction mixture is subsequently heated to a temperature of 130°C and stirred. After reacting for 1 h, infrared analysis of a sample of the reaction mass shows that the reaction for the masking of the isocyanate functional groups is complete. The disappearance of the band signifying the isocyanate functional groups at 2272 cm<sup>-1</sup> is observed.

10 The product is then poured onto a plate and then left to cool. The product is subsequently milled at a temperature of -10°C.

At ambient temperature, the milled product behaves like an instant adhesive (sticky like pitch) and does not give a powder which can be handled under conventional industrial conditions, in particular at ambient temperature (approximately 20°C).

The measured Tg of the product is 10°C.





## DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITE DE COOPERATION EN MATIERE DE BREVETS (PCT)

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<p>(21) Numéro de la demande internationale: PCT/FR99/01858</p> <p>(22) Date de dépôt international: 28 juillet 1999 (28.07.99)</p> <p>(30) Données relatives à la priorité: 98/09699 29 juillet 1998 (29.07.98) FR</p> <p>(71) Déposant (pour tous les Etats désignés sauf US): RHO-DIA CHIMIE [FR/FR]; 25, quai Paul Doumer, F-92408 Courbevoie Cedex (FR).</p> <p>(72) Inventeurs; et (75) Inventeurs/Déposants (US seulement): BERNARD, Jean-Marie [FR/FR]; Route du Large, Saint-Laurent D'Agy, F-69440 Mornant (FR). VOGIN, Bernard [FR/FR]; 17, impasse des Framboisiers, F-69630 Chaponost (FR).</p> <p>(74) Mandataire: RICALENS, François; Rhodia Services, Direction de la Propriété Industrielle, 25, quai Paul Doumer, F-92408 Courbevoie Cedex (FR).</p>		<p>(81) Etats désignés: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KG, KP, KR, KZ, LC, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, SL, TJ, TM, TR, TT, UA, US, UZ, VN, YU, ZA, brevet ARIPO (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), brevet eurasién (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet européen (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), brevet OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Publiée Avec rapport de recherche internationale.</p>
<p>(54) Title: <u>ISOCYANATE COMPOSITION CONTAINING A MASKED AND AN UNMASKED ISOCYANATE AND THEIR USE FOR COATING</u></p> <p>(54) Titre: COMPOSITION ISOCYANATE COMPORTANT UN ISOCYANATE MASQUE ET UN NON MASQUE ET LEUR UTILISATION DANS UN REVETEMENT</p> <p>(57) Abstract</p> <p>The invention concerns an isocyanate composition useful for applying powder paints. Said composition is characterised in that it contains a masked isocyanate compound and an unmasked cycloaliphatic isocyanate compound. The invention is applicable in the chemistry of paints.</p> <p>(57) Abrégé</p> <p>La présente invention a pour objet une composition isocyanate utile pour les applications en peintures poudre. Cette composition se définit en ce qu'elle comporte un composé isocyanate masqué et un composé isocyanate cycloaliphatique non masqué. Application à la chimie des peintures.</p>		

CLAIMS

1. An isocyanate composition of use in powder paint applications, characterized in that it  
5 comprises a masked isocyanate compound and a nonmasked cycloaliphatic isocyanate compound.

2. A composition as claimed in claim 1, characterized in that said masked isocyanate compound is at least partially aliphatic.

10 3. A composition as claimed in claims 1 and 2, characterized in that said masked isocyanate compound exhibits an aliphatic backbone which comprises, in its backbone, at least one di- or polymethylene linkage.

15 4. A composition as claimed in claims 1 to 3, characterized in that said masked isocyanate compound does not exhibit masked isocyanate functional groups which are carried by an endocyclic cycloaliphatic carbon.

20 5. A composition as claimed in claims 1 to 4, characterized in that said masked isocyanate compound results from a polymethylene diisocyanate monomer, from one of the (co)oligomers of the latter or from one of its (co)oligocondensates.

25 6. A composition as claimed in claim 5, characterized in that said polymethylene diisocyanate

monomer is tetra-, penta- or hexamethylene diisocyanate, substituted at the most once.

7. A composition as claimed in claims 1 to 6, characterized in that said (co)oligomer or  
5 (co)oligocondensate comprises one or more imidazolidinedione, isocyanuric, biuret, allophanate or polyol carbamate functional groups.

8. A composition as claimed in claims 1 to 7, characterized in that said nonmasked cycloaliphatic  
10 isocyanate exhibits a Tg at least equal to approximately 40°C.

9. A composition as claimed in claims 1 to 8, characterized in that said cycloaliphatic isocyanate is an oligomer of a cycloaliphatic monomer.

15 10. A composition as claimed in claims 1 to 9, characterized in that said cycloaliphatic isocyanate results from the homo- or from the heterotrimerization of a cycloaliphatic monomer.

11. A composition as claimed in claims 1 to 20 10, characterized in that at least one, advantageously two, isocyanate functional group is distant from the closer ring by at most one carbon and is preferably connected directly to it.

12. A composition as claimed in claims 1 to 25 11, characterized in that said nonmasked isocyanate compound exhibits at least one, advantageously two,

isocyanate functional group is chosen from secondary, tertiary or neopentyl isocyanate functional groups.

13. A composition as claimed in claims 1 to 12, characterized in that the (FI/MI) ratio by mass of the free isocyanate compound to the masked isocyanate compound is at least equal to 0.1, advantageously to 0.2, preferably to 0.3.

14. A composition as claimed in claims 1 to 13, characterized in that the ratio (in equivalents) of the free isocyanate functional groups to the masked isocyanate functional groups is at most equal to approximately 1, advantageously to 1.0, preferably to 0.7.

15. A process for the preparation of a composition as claimed in claims 1 to 14, characterized in that the free isocyanate is mixed in the molten masked isocyanate.

16. The use of cycloaliphatic compounds with a glass transition temperature ( $T_g$ ) at least equal to 40°C for raising the glass transition temperature ( $T_g$ ) of masked aliphatic isocyanate.

17. The use of a composition as claimed in claims 1 to 15 as ingredient of a coating, advantageously in the powder form.

RN98105

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**Abstract of the Disclosure****ISOCYANATE COMPOSITION COMPRISING A MASKED ISOCYANATE**

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**AND A NONMASKED AND THEIR USE IN A COATING**

The invention concerns an isocyanate composition useful for applying powder paints. Said composition is characterized in that it contains a masked isocyanate compound and an unmasked cycloaliphatic isocyanate compound. The invention is applicable in the chemistry of paints.

20

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My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**ISOCYANATE COMPOSITION COMPRISING A MASKED ISOCYANATE AND A NONMASKED  
AND THEIR USE IN A COATING**

the specification of which (check only one item below):

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Serial No. \_\_\_\_\_

on \_\_\_\_\_

and was amended

on \_\_\_\_\_ (if applicable)

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I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

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France	98/09699	29 July 1998	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
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